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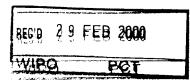
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Application No.

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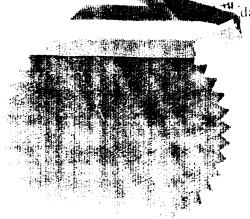
8 February, 1999

**Applicant** 

UNIVERSITY COLLEGE CORK, a university established by Statute of the Republic of Ireland of

College Road, Cork, Ireland.

day of February, 2000.



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# REQ ST FOR THE GRANT OF A PA

### PATENTS ACT, 1992

The Applicant(s) named here the grant of a pa	in hereby request(s) tent under Part II of the Act
the grant of a shoon the basis of the informati	ort-term patent under Part III of on furnished hereunder.
1. Applicant(s)	
<u>Name</u>	UNIVERSITY COLLEGE CORK
Address	College Road, Cork, Ireland.
Description/Nationality	A university established by Statute of the Republic of Ireland.
2. <u>Title of Invention</u>	"Complexing agents"
Declaration of Priority on ba application(s) for same inves	

Country in or for

which filed

4. <u>Identification of Inventor(s)</u>

Previous filing date

Name(s) of person(s) believed by Applicant(s) to be the inventor(s)

JEREMY DENIS GLENNON and STEPHEN JOHN HARRIS Address

Kileden, Nova Court, Carrigaline, County Cork, Ireland, an Irish citizen, and 10 Broadford Crescent, Ballinteer, Dublin 16, Ireland, a British subject, respectively.

Filing No.

	The applicant by virtue of	t has derived the a Deed of Assign	e right to be nment dated Fe	granted a February 8. 1	Patent from th	ne inventors
6.	Items accompa	anying this Request	- tick as appropr	<u>iate</u>		
	(i) X	Prescribed filing for	ee (£ 50.00 )			
	(ii)	Specification cont	aining a descript	ion and claim	S	
	X	Specification cont.	aining a descript	ion only		
		Drawings referred	to in description	n or claims		
	(iii)	An abstract				
	(iv)	Copy of previous a	application(s) wh	nose priority is	s claimed	
	(v)	Translation of prev	vious application	whose priorit	y is claimed	
	(vi)	Authorisation of A below if this Requi	•	-	s))	
7.	Divisional App	olication(s)				
	The following	information is applic	cable to the pres	ent application	which is made	under Section 24 -
	• •	ation No: Date:				
3.	Agent					
		is authorised to act a patent to which this				nted -
)	<u>Name</u>			Address		
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5. Statement of right to be grant in patent (Section 17 (2) (b) )



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### "Complexing Agents"

This invention relates to a complexing agent and in particular to fluorinated thiourea complexing agents and fluorinated thiourea complexing agents for use in the extraction of metals such as gold.

Complexing agents are widely employed in the extraction and recovery of metals such as gold, silver and the like.

For example, gold is a soft yellow metal having a melting point of 1063°C with the highest ductility and malleability of any element. It is chemically unreactive and is not attacked by oxygen or sulphur but reacts readily with halogens or with solutions containing or generating chlorine such as "aqua regia". Its most common compounds exist in the (I) and (III) oxidation states.

Heretofore, the extraction of gold from ore and from other solid phases such as in solid phase extraction has been commonly carried out by using cyanide or thiourea as reagents. In the most commercially important method for gold extraction finely crushed ore is treated with sodium cyanide in the presence of oxygen to give a sodium gold cyanide complex, which is typically absorbed onto activated carbon. The sodium gold cyanide complex can be re-extracted later and reduced to the metal, (H. Schmidbaur, Interdisciplinary Science Reviews, 17 (3), 213,1992 and A. Sigel and H. Sigel in "Handbook on Metals in Clinical and Analytical Chemistry", Ed. H.G. Seiler, 1994 p388) viz:

$$4Au + 8CN^{2} + O_{2} + 2H_{2}O \longrightarrow 4[Au(CN)_{2}]^{2} + 4OH^{2}$$

However, treatment with sodium cyanide is environmentally unfriendly while the efficiency of the reaction can be poor and variable according to the ore type.

Accordingly, other methods of gold extraction have been developed e.g. thiourea based extraction. Thiourea based extractions enjoy the advantages of higher leaching efficiency, rapid leaching, adaptation to a variety of refractory ores and reduced toxicity to the environment. Accordingly, thioureation is an attractive procedure for the extraction of both gold and silver.

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For example, it has been demonstrated (C.K. Chen, T.N. Lung and C.C. Lung and C.C. Wan, Hydrometallurgy, <u>5</u>, 207, 1980) that employing Fe<sup>3+</sup> as oxidant in acid solutions resulted in leaching with thiourea which was ten times faster than leaching with sodium cyanide, <u>viz:</u>

$$Au + Fe^{3+} + NH_2 - C - NH_2 - H_2N$$
 $C=S-Au-S=C$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 

However, excessive consumption of thiourea in the process has limited its industrial application.

Various attempts have been made to reduce thiourea consumption. For example in order to reduce thiourea consumption in gold extraction it has been suggested (C.C. Kenna, Gold Bull, <u>24(4)</u>, 126, 1991) that the complexing of ferric ions could be utilised

in reducing their oxidative power to a level where oxidation of gold still proceeded at an acceptable rate while oxidation (and consumption) of thiourea was greatly reduced.

U.S. Patent Specification No. 5126038 also discloses that alkyl hydroxamic acids or their salts may be used to improve extraction of precious metals, including gold, from sulphide ores in combination with standard sulphide ore collectors such as xanthates, substituted thioureas and the like.

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G. Zuo and M. Muhammed, Separation Science and Technology, <u>25(13-15)</u>, 1785, 1990 also describe the synthesis and characterisation of a family of thiourea based reagents for the extraction of Au(III) and Ag(I) ions through complex formation from HCI solutions and also disclose the synthesis of several co-ordinating polymers by grafting thiourea functional groups onto commercial macroporous polystyrene polymer matrices.

In order to avoid the use of thioureas, azacrowns have also been used to facilitate transport of NaAu(CN)<sub>2</sub> into an organic phase from an aqueous phase (M. Tromp, M. Burgard, M.J.F. Leroy and M. Prevost, J. of Membrane Science, <u>38</u>, 295, 1988). In addition, Izatt et al., (R.L. Bruening, B.J. Tarbet, T.E. Krakowiak, M.L. Bruening, R.M. Izaat and J.S. Bradshaw, Anal. Chem., <u>63(10)</u>, 1014, 1991 and R.L. Bruening, B.J. Tarbet, K.E. Krakowiak, R.M. Izatt and J.S. Bradshaw, J. Heterocyclic Chem., <u>27</u> 347, 1990) have developed silica gel bound thia – macrocycles which have shown high selectivity for Au(III).

Supercritical fluid extraction (SFE) has developed into an attractive alternative to conventional solvent extraction to recover organic compounds from solids in particular. A useful fluid for SFE work is carbon dioxide due to its moderate critical constants ( $T_c = 31.1 \, ^{\circ}\text{C}$ ,  $P_c = 72.8 \, \text{atm}$ ), inertness, ease of availability, low cost and ease of final removal. However, direct extraction of metal ions, by supercritical  $CO_2$  is very inefficient due to the charge neutralisation required and weak solute-solvent interactions.

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Supercritical fluid extraction of gold has been reported by S. Wang, S. Elshani and C.M. Wai, Anal. Chem., <u>67</u>, 919 1995 where Au(III) ions were extracted by bistriazalocrowns from wet solid matrices using supercritical CO<sub>2</sub> modified with methanol. Neutral gold complexes were formed due to the presence of triazalo protons:

which were soluble in modified SF-CO<sub>2</sub>. The presence of the triazolo protons was necessary for the extraction of the metal ions to give a neutral metal ion-ligand complex:

$$N - N - N$$
 $N - N - N$ 
 $N - N - N$ 
 $N - N - N$ 

and no extraction was possible without methanol modifier or water in the solid phase. Supercritical CO<sub>2</sub> has also been utilised (E.O. Out, Separation Science and Technology 32,6, 1107, 1997) to elute gold in the form of NaAu(CN)<sub>2</sub> previously adsorbed on activated charcoal employing tributylphosphate to facilitate charge neutralisation. However, the presence of water in the solid phase was required for the extraction while as indicated previously the use of cyanide is undesirable for environmental and safety reasons.

An object of the invention is to overcome the problems of the prior art.

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A further object of the invention is to provide a complexing agent or ligand for gold extraction.

A still further object of the invention is to provide a method for extracting gold which overcomes the problems of the prior art.

According to the invention there is provided a thiourea having the general formula:

$$\begin{array}{c|c}
S \\
R^{1} \parallel \\
N-C-N \\
R^{3}
\end{array}$$

characterised in that R¹ and R² comprise a fluorine containing alkyl, alkaryl, aryl or substituted derivatives thereof and R³ and R⁴ are selected from the group comprising H, alkyl, aryl, alkaryl or substituted derivatives thereof. In one aspect of the invention R³ and R⁴ are selected from the group comprising fluorine containing alkyl, aryl, alkaryl or substituted derivatives thereof. The fluorinated derivatives of the invention are extremely useful for analytical assays for the selective determination of gold levels, and for gold recovery.

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Preferably, R<sup>1</sup> comprises

$$CF_3$$
,  $R^2$  comprises— $CH_2$ — $CF_2$ — $CF_2$ — $CF_3$ 

R<sup>3</sup> comprises H and R<sup>4</sup> comprises H.

15 Alternatively, R<sup>1</sup> comprises

$$CF_3$$
,  $R^2$  comprises —  $CH_2CF_3$ ,  $CF_3$ 

R³ comprises H and R⁴ comprises H.

The invention also extends to a method of producing a fluorinated thiourea comprising reacting a compound of general formula

with a compound of general formula

$$R^2$$

10

where both R<sup>1</sup> and R<sup>2</sup> contain fluorine.

The invention also relates to a method for extracting gold from a matrix comprising treating the matrix with a thiourea having the general formula

$$\begin{array}{c|c}
S \\
R^{1} & \parallel \\
N-C-N & R^{2}
\end{array}$$

where R¹ and R² comprise a fluorine containing alkyl, alkaryl, aryl or substituted derivatives thereof and R³ and R⁴ are selected from the group comprising H, alkyl, aryl or substituted derivatives thereof and subjecting the matrix to supercritical fluid extraction.

Preferably, the supercritical fluid extraction comprises CO<sub>2</sub> supercritical fluid extraction.

10 Preferably, R<sup>1</sup> comprises

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$$CF_3$$
,  $R^2$  comprises— $(CH_2)a$ — $(CF_2)_b$ — $CF_3$ 

 $R^3$  comprises H and  $R^4$  comprises H where  $a \ge 1$  and b = 0 - 6.

In one embodiment of the invention the gold is extracted in the presence of an oxidant. Suitably, the oxidant comprises Fe (III) ions.

Advantageously, b > 3.

The invention also extends to the use of a fluorinated thiourea of the general formula

$$\begin{array}{c|c}
S \\
R^{1} & R^{2} \\
N-C-N & R^{4}
\end{array}$$

where R¹ and R² comprise a fluorine containing alkyl, alkaryl, aryl or substituted derivatives thereof and R³ and R⁴ are selected from the group comprising H, alkyl, aryl, alkaryl or substituted derivatives thereof in the extraction of gold from a matrix.

Surprisingly, it has been found that fluorinated thioureas of the general formula:

10

$$CF_3$$
 $S$ 
 $II$ 
 $NH-C-NH-(CH_2)_a-(CF_2)_b-CF_3$ 
 $CF_3$ 

a ≥ 1

b = 0-6

efficiently extract Au(I) and Au(III) from a solid matrix in unmodified supercritical CO<sub>2</sub> and furthermore may extract gold from a solid containing gold in its elemental form in the presence of an oxidant. Fe(III) ions are particularly suitable as oxidants. The addition of modifiers or protons is not required and extraction can be carried out using fluorinated thioureas alone.

In contradistinction, thiourea itself does not form a neutral complex with gold i.e. gives Au  $[SC(NH_2)_2]_2^{+}$ .

5 In a preferred embodiment of the invention b> 3.

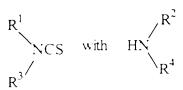
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The fluorinated thioureas of the invention have a high solubility in supercritical CO<sub>2</sub> and are extremely efficient at solubilising and carrying gold for the purposes of extraction, recovery or impregnation.

The fluorinated thioureas can be synthesised in a simple one-step process by the reaction of:

with the appropriate amine NH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>b</sub>CF<sub>3</sub> where b= 0 or 2 or 6 in a room temperature (exothermic) reaction and recrystallisation from petroleum ether (100-120) to give colourless products in 62 to 81% yields.

The compositions of the invention can therefore be formed by the simple reaction of



where both R<sup>1</sup> and R<sup>2</sup> contain fluorine.

- Various embodiments of the invention will now be described by way of Example only, having regard to the following drawing and examples in which:
  - Fig. 1 is a block diagram indicating the amount of gold extracted from a geological sample on repetitive extraction with Fe(III) as oxidant.

### Comparative Example

10

$$CF_3$$
 $NH - C - NH_2$ 
 $CF_3$ 

The aforementioned fluorinated thiourea is known from the prior art and is commercially available from FLUOROCHEM (Trade Mark).

#### Example 1

$$CF_3$$
 $S$ 
 $\parallel$ 
 $NH-C-NH-CH_2-CF_2-CF_3$ 
 $CF_3$ 

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To 0.518 g (0.0026mole) 1H, 1H-heptafluorobutylamine (Fluorochem (Trade Mark) Product FO4396) in a round bottom flask was added 0.705g (0.0026mole) 3,5-di(trifluoromethyl) phenylisothiocyanate (Fluorochem (Trade Mark) Product F03115B). After stirring for one minute the miscible liquids solidified to a colourless solid in an exothemic reaction. After the reaction mixture had cooled it was allowed to stand for 1 hour at room temperature and the product was recrystallised from petroleum ether (100-120) to give 0.972 g of pure product (80% yield) as colourless crystals, mp 130-132°C.

15 Elemental Analysis for C<sub>13</sub>H<sub>7</sub>N<sub>2</sub>SF<sub>13</sub>:

Calculated: C: 33.20, H: 1.50, N:5.96, Found C: 33.05, H: 1.49, N: 6.12%

### Example 2

$$CF_3$$
 $\parallel$ 
 $CF_3$ 
 $\parallel$ 
 $CF_3$ 
 $\parallel$ 
 $CF_3$ 

To 0.705g (0.0026 mole) 3,5-di(trifluoromethyl)-phenylisothiocyanate in a round bottom flask cooled in an ice bath, with stirring under nitrogen, was added 0.281g (0.00283 mole) trifluoroethyl amine (Aldrich (Trade Mark) product 26,904-2). After a short period an exothermic reaction occurred to give a colourless solid. The reaction mixture was then allowed to warm to room temperature and was left for 1 hour under a stream of dry nitrogen to remove excess volatile amine (bp 36°C). The solid was recrystallised from petroleum ether (100-120) to give a pure product as fluffy colourless crystals 0.60g (62% yield).

Elemental Analysis for C<sub>11</sub>H<sub>7</sub>N<sub>2</sub>SF<sub>9</sub>:

10 Calculated: C: 35. 64, H: 2.04, N:7.55, Found C: 35.94, H: 2.20, N: 7.73%

#### Example 3

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$$CF_3$$
 $\parallel$ 
 $NH-C-NH-CH_2(CF_2)_6CF_3$ 
 $CF_3$ 

To 3.28 (0.0121 mole) 3,5-di(trifluoromethyl) – phenylisothiocyanate in a round bottom flask was added 4.82g (0.0121 mole) 1H, 1H – perfluoro-octylamine Lancaster (Trade Mark) product 16845 with stirring. An exothermic reaction rapidly ensued and after cooling to room temperature was allowed to remain for 2 hours. The white solid product was recrystallised from 100-120°C petroleum ether to give 6.50g pure product (81% yield) as a colorless crystalline solid.

Elemental Analysis: C<sub>17</sub>H<sub>7</sub>N<sub>2</sub>SF<sub>21</sub>

Calculated: C:30.46, H:1.05, N:4.18; Found: C:30.60, H:1.16, N:4.40%

### Example 4

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The solubility of the ligand of the comparative Example in supercritical CO<sub>2</sub> was compared with the solubilities of the ligands of Examples 1 and 2 in supercritical CO<sub>2</sub>.

A weighed amount of the ligand of the comparative Example of approximately 60 mg was placed in a glass tube (2cm x 0.5cm i.d.) and plugged with glass wool at both ends. The glass tube was placed inside the extraction vessel and statically extracted for 30 minutes. The inlet valve for SF-CO<sub>2</sub> was then closed and the outlet valve opened into a collecting solution. The loss of weight of the glass tube after SFE corresponded to the solubility of the ligand in 2.2 ml 100% SF-CO<sub>2</sub>. The procedure was carried out at 60°C and two different pressures namely 200 and 300 atmospheres.

15 Most of the ligand appeared to remain in the glass tube indicating poor solubility in SF-CO<sub>2</sub>.

### Solubility of the ligand of Example 1 in supercritical CO<sub>2</sub>:

The procedure outlined above was repeated for the ligand of Example 1. Solubilities of 1.81 x 10<sup>-2</sup>M at 60°C, 200 atm, and 3.38 x 10<sup>-2</sup>M at 60°C, 300 atm were recorded indicating an extremely high solubility as compared with that of the prior art.

# Solubility of the ligand of Example 2 in supercritical CO<sub>2</sub>:

The procedure was repeated for the ligand of Example 2. Solubilities of

>2 x  $10^{-2}$ M at  $60^{\circ}$ C, 200 atm, and > 4 x  $10^{-2}$ M at  $60^{\circ}$ C, 300 atm were recorded again indicating an extremely high solubility as compared with the fluorinated thiourea of the comparative Example.

A number of experiments were carried out to demonstrate the extraction efficiencies of the fluorinated thioureas of the invention.

Example 5 (comparative): Supercritical Fluid Extraction of Au(III) as AuCl<sub>4</sub> using the compound of the comparative Example.

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Gold Au(III) extraction by the ligand of the comparative Example was investigated employing a BDH Gold (III) standard containing 1000 ppm Au(III) (aqueous AuC1<sub>4</sub><sup>-</sup>). Thus 60 µl of solution Au(III) containing 3.05 x 10<sup>-7</sup> moles Au(III) was applied to a 3cm diameter filter paper. The filter paper was allowed to dry and then placed in a glass tube (2cm x 0.5cm i.d.), plugged with glass wool at both ends. 20mg of ligand of the comparative Example (in excess of over 200 fold over Au(III) level) was then placed in the same glass tube and plugged with glass wool. The temperature of the extraction vessel was then set at 60°C and the pressure was varied as indicated in Table 1.

- 20 The extraction vessel was statically extracted for 20 minutes and then dynamically extracted into a collecting solvent of 4 ml methanol for 15 minutes (0.8 ml CO<sub>2</sub>/minute flow rate). The methanol solution was then made up to 10 ml using additional methanol. Levels of gold in solution were then determined by atomic absorption spectroscopy. The procedure was carried out at different pressures from 200-400 atm.
- 25 The following extraction percentages were obtained:

T	۱D	1	_	1
	٩п		_	-1

	Pressure SF-CO <sub>2</sub> (atm)	Atomic Absorption (A.U.)*	Extraction (%)
5	200	0.000	0
	250	0.000	0
	300	0.001	0.3
	350	0.000	0
	400	0.024	6.7
10			

\* The % extraction is calculated with reference to the Atomic Absorption reading obtained for 10ml of collecting solution spiked directly with 60μl of the 1000ppm Au(III) standard. (For example for the data presented in Table 1 a standard of 60 μg/10 ml = 6ppm Au, gave an absorption value of 0.359, representing 100% extraction. Note such recordings of standard values were carried out alongside the sample analysed on the

400 atm was the only pressure of SF-CO $_2$  to give detectable Au(III) extraction. In all runs most of the ligand appeared to remain in the glass tube indicating poor solubility in SF-CO $_2$ .

#### Example 6 (comparative)

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same day.)

The procedure in Example 5 was repeated except the temperature of the extraction procedure was varied from 60-120°C, while maintaining the pressure of the extractor at 400 atm. The following results were obtained:

T	Α	В	L	Ε	2
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	Temperature	Atomic Absorption	Extraction
	(°C)	(A.U.)*	(%)
_			
5			
	60	0.027	8.8
	80	0.002	0.7
	100	0.006	2.0
	120	0.005	1.6
10			

<sup>\*</sup> A standard of 6ppm Au, gave an absorption value of 0.305 = 100%

The % extraction of gold remained low.

### 15 Example 7

The procedure in Example 6 was repeated with the ligand from Example 1 being used in place of the ligand of the Comparative Example. The following % extraction values were obtained at differing pressures for extraction of Au(III):

20

25

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TABLE 3

	Pressure SF-CO <sub>2</sub>	Extraction
	(atm)	(%)
5		
	200	61.2
	250	92.7
	300	83.7
10	350	75.3
	400	78.1

Percentage extraction with the ligand of the invention was therefore excellent at 92.7% compared with the poor extraction (<10%) with the ligand of the comparative Example.

### Example 8

Reduction of Au(III) to Au(0) was accomplished by treatment with hydroxylamine hydrochloride followed by sodium hydroxide.

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The procedure in Example 7 was repeated except the conditions were altered to 60°C at 250 atm. The 60µl of AuCl₄ was replaced by 60µl of a well mixed even suspension of Au(0) applied to the filter paper which was allowed to dry to give a black-blue colour. The collected methanol solutions, made up to 10 ml as before, were analysed by Atomic Absorption Spectroscopy as before, giving the following % extraction values:

TABLE 4

_	Pressure SF-CO <sub>2</sub>	Atomic Absorption	Extraction	
5	(atm)	(A.U)*	(%)	
	200	0.001	~ 0.0	
	250	0.002	~ 0.0	
10	300	0.001	~ 0.0	
	350	0.002	~ 0.0	
	400	0.002	~ 0.0	

Accordingly, the ligand of Example 1 did not extract Au(0). Moreover, at the end of the runs the blue-black colour of Au(0) remained on the filter paper and no ligand remained in the tube. However, as described further below the gold could be extracted following oxidation of Au(0) to either Au(I) or Au(II).

### 20 Example 9

The procedure in Example 8 was repeated but 40mg of solid Au(0) was used in place of the Au(0) suspension deposited on the filter paper to give an identical result to Example 8.

### Example 10

The procedure of Example 9 was repeated utilising 20 mg of the ligand Example 1 except 11.2 mg of solid Au(0) was used and on two occasions the Au(0) was first oxidised to Au(I) by spiking 60 µI of Fe(III) (1000 ppm stock solution) onto the solid Au(0) directly and then allowed to dry. In the case where Fe(III) had been added when the collected methanol solution (as usual made up to 10 ml) was analysed by atomic absorption a large signal was obtained (0.252) and (0.253) indicating extraction of Au(I). Fe(III) was the limiting reagent as:

$$Fe(III) + Au(0) \rightarrow Fe(II) + Au(I)$$

and therefore  $60\mu I$  1000ppm Fe(III) (1.075 $\mu$ mole) is equivalent to  $212\mu I$  of 1000ppm Au(I) (0.2 mg Au).

15 Table 5 below outlines the results obtained following application of Fe(III):

### TABLE 5

Sample	Atomic Absorption	Extraction
	(A.U.)*	(%)
11.2mg Au(0)	0.001	0
+ 20mg ligand of	0.001	O .
Example 1		
11.2 mg Au(0)	0.252	20.0
+ 60 µl Fe(III) + 20mg		
ligand of Example 1		
11.2 mg Au(0)	0.253	20.0
+ 60 µl Fe(III) + 20mg		
ligand of Example 1		

A 212µl aliquot of 1000 pp, Au(III) standard solution gave an absorption value of 1.263 20 = 100%.

Accordingly, Au(0) has been successfully oxidised by Fe(III) to give Au(I) which has been extracted with the fluorinated ligand of the invention. That only 20% of the theoretically freed gold (by Fe) was finally detected by atomic absorption is not surprising in view of the fact that the Fe(III) was applied as a 1000ppm aqueous nitrate solution to the solid Au(0) on the filter paper without thorough mixing.

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Nevertheless, the method can be employed successfully as a qualitative test for Au(0).

### Example 11

The procedure of Example 7 was repeated employing the ligand of Example 2 in place of the ligand of Example 1 and utilising 50µl Au(III) standard solution in place of 60µl to give the following % extraction results at differing pressures of SF-CO<sub>2</sub> at 60°C.

TABLE 6

10	Atmosphere SF-CO <sub>2</sub>	Extraction (%)
15		
	200	41
	250	51
	300	22
	400	14
0		

### Example 12

The procedure of Example 11 was repeated except Au(III) standard was replaced by
5.7 mg solid Au(0) and extraction was determined under previously optimised
conditions 60°C/250 atm SF-CO<sub>2</sub>. Table 7 summarises the results:

### TABLE 7

Sample Extraction

(%)

Au(O) + ligand ~ 3

### Example 13

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Above Example 12 was repeated except that 30µl 1000 ppm Fe(III) standard (aqueous nitrate) was spiked onto the Au(0) prior to extraction with SF-CO<sub>2</sub> (250atm/60°C).

Table 8 below summarises the results obtained.

TABLE 8

Sample Extraction

(%)

Au(O) + 30µl Fe(III) 57
+ 20mg ligand

The above percentage is based on the Fe(III) oxidisable quality of gold i.e. Fe(III) is the limiting reagent.

57% of the "freed" gold Au(I) was therefore extracted with the fluorinated ligand of the invention.

### Example 14

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Example 13 was repeated but Au(0) was replaced by a 5mg geological sample containing trace Au(0) (2ppm  $\pm$  0.3ppm). Extraction with SF-CO<sub>2</sub> was carried out with repetitive additions (30mg) of ligand and repetitive additions of 50 $\mu$ l Fe(III) standard to give the following results:

		TABLE 9	
	Sample	Atomic Absorption	Extraction
10		(A.U.)*	(%)
	Geological sample	0.000	-
	alone		
15			
	Geological samples		
	and ligand and Fe(III)		
	Extraction # 1	0.005	5.0%
	Extraction # 2	0.038	38.0%
20	Extraction # 3	0.025	25.0%
	Extraction # 4	0.011	22.0%
	Extraction # 5	0.006	12.0%

44

The collection volumes up to Extraction # 2 were 5ml and for Extraction #4 to #5 were 10ml. The results achieved were within accepted ranges of variance for trace analyses.

The gold can be extracted from geological samples when prior treatment with an oxidant, such as Fe(III) is used. Fig. 1 shows the amount of gold extracted from the geological sample, on repetitive extraction with Fe(III) as oxidant.

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The linear fluorinated thioureas of the invention therefore have the unexpected property of extracting Au(III) in supercritical CO<sub>2</sub>. In addition Au(I) may be extracted from Au(0) (in its elemental state) by prior treatment with Fe(III). Finally, Au(I) can also be extracted from geological sample containing gold also by prior treatment with Fe(III). The complexing agents and extraction methods of the invention are highly efficient and do not require the use of cyanides. In addition, the fluorinated thioureas of the invention facilitate the extraction of gold without excessive thiourea consumption.

Moreover, extraction of gold using fluorinated thioureas and supercritical fluid can be effected without requiring the addition of modifiers, protons and the like.

The invention is not limited to the embodiments herein described which may be varied in construction and detail.

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Amount of Au Extraction vs. Extraction No.

